A molecular dynamics simulation study of oxygen within hydrated Nafion-117 for fuel cell application

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Abstract

Fuel cells have several obstacles before they can see widespread use. Nafion, the current most successful polymer for use in polymer electrolyte fuel cells (PEMFCs) has been characterized by numerous other studies both experimental and computational. This study determines the, until now unexplored, behavior of oxygen within a Nafion system hydrated at 10 and 20wt%. The systems are equilibrated at temperatures of 353, 363, 373, and 383 Kelvin. Then the structure and transport characteristics of the system are explored using pair correlation and mean square displacement functions. As the hydration increased, the oxygen molecules became more coordinated with water resulting in a decrease in the diffusion coefficient of oxygen within the system. This has important implications in the efficiency of the fuel cell. This data furthers the pursuit of a more perfect polymer membrane for use in fuel cells.

1 Introduction

Fuel cell technology has the capability to revolutionize the way automobiles are powered. Through their many advantages, environmental friendliness chief among them, they are likely to set the pace for a future of more conscientious energy use.

Fuel cells have numerous advantages over the current methods of automobile power production. The most often cited is that, unlike a combustion engine, a fuel cell would produce no harmful green house gases. In fact, the only byproduct that occurs in the "exhaust" of a fuel cell is clean water [1]. Another major advantage is freedom from fossil fuel dependence.

Whereas petroleum is a scarce resource, unevenly distributed throughout the world, fuel cells use very common chemicals as their energy source, commonly either manufactured hydrogen gas or methanol.

The fact that fuel cells are not currently prevalent within the automotive industry stems from the difficult conditions under which they must operate . Fuel cell membranes are very sensitive to temperature; current materials are not stable enough to overcome fluctuations present in a mobile environment. Mehta concludes that many of the current fuel cell membranes are ill-suited for automobile applications for a number of reasons, such as expense and poor durability [6]. Materials scientists are currently searching for the solution, starting with experimental studies. There is an extensive amount of information about Nafion, due to its success in the laboratory setting, which Mauritz has compiled [5]. As computational power continues to increase, the idea of using theoretical modeling to find an ideal membrane becomes more feasible. New protocols must be formulated to allow the sharing of knowledge between groups and help the field progress. These protocols are currently in the developmental stage. With this study we hope to further the field's knowledge of Nafion-117, as well as shape the methods by which research in this area is performed.

1.1 Fuel Cell Basics

In fuel cells, as in batteries, a potential difference is created between the anode and cathode of the cell through a chemical reaction. In batteries this reaction is commonly between a metal and electrolyte, causing freed electrons to travel to the anode through some electrical load, doing work, while cations travel through the electrolyte to the cathode.

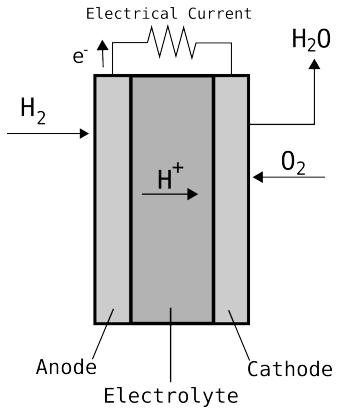

Figure 1: Fuel Cell schematic

The power producing mechanism of a fuel cell is essentially the same as that of batteries,

except a fuel cell's anode may be replenished. Unlike a battery, the consumed portion, the "fuel", of the anode side of the fuel cell can be replaced without major reconstruction of the cell. The most popular fuel choices for fuel cells today are hydrogen gas, H_2, and methanol, CH_3OH, catalyzed at the anode to provide protons and electrons.

Nafion is currently most successful material for use in polymer electrolyte membrane fuel cells (PEMFCs) due to its high proton conductivity and excellent chemical stability. Jang et al. described the effect of monomeric sequence, e.g. blocky vs random, on the transport properties of bulk Nafion using molecular dynamics simulation [4]. The equilibrium structure of the hydrated Nafion system has been the topic of a great deal of research. The prevailing theory is that water forms clusters within the amorphous polymer due to the hydrophilic nature of the polytetrafluoroethylene backbone of the Nafion [2]. These clusters have been examined through simulation as well as experimentally using infrared absorption and other techniques [3]. There are several models to describe the transport and distribution of polymer, water, and protons within Nafion. One of the most popular is the Yeager Three-Phase model. In this model, a hydrated nation membrane forms three distinct phases at equilibrium: a phase consisting of the hydrophilic clusters of water-solvated ion groups, a phase of the hydrophobic tetrafluoroethylene backbone, and a middle interfacial phase of unclustered ions and a large amount of free volume[7]. The intent of this study is to determine in which of these three phases the oxygen molecule is most likely to be found in bulk Nafion.

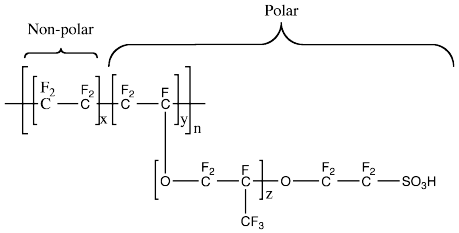

Figure 2: Nafion. The equivalent weight, 117, indicates the number of reactive groups per chain.

2 Objective

Currently, there has not been a simulation study performed with oxygen present in the membrane even though this condition will certainly occur during fuel cell applications. This study investigates the hydrated Nafion membrane with the addition of oxygen molecules using full atomistic MD simulation to describe the nanophase-segregated structure.

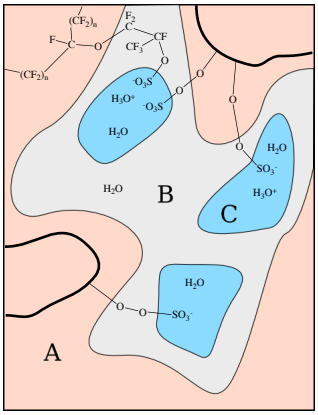

Figure 3: A depiction of the Yeager Three Phase model with A: Hydrophobic groups, B: Free Volume, and C: Hydrophilic groups.

3 Simulation Details

This study uses a fully atomistic model of Nafion-117. To determine the effect of hydration on the oxygenated systems, two systems are prepared using 10 wt % as well as 15 water molecules per sulfonate group. No external electric field is applied in this study.

3.1 Force field and simulation parameters

The DREIDING force field describes the interactions between the majority of the particles in this simulation, with the exception of the water molecules modeled with the F3C force field. The net force field of the system is described by:

$$E_tot = E_{vdW} + E_Q + E_{bond} + E_{angle} + E_{torsion} + E_{inversion}$$

with $E_tot, E_{vdW}, E_Q, E_{bond}, E_{angle}, E_{torsion}, E_{inversion}$ representing the total energy, van der Waals, electrostatic, bond stretching, angle bending, torsion, and inversion components, respectively.

The charge equilibration method reproduces the Mulliken charges of small molecules and is used to assign individual atomic charges for Nafion. Water uses the F3C model atomic charges. The particle -particle particle-mesh method calculates the electrostatic interactions.

LAMMPS from Plimpton et al. at Sandia performs the MD simulations and annealing steps, with modifications for custom force fields. Classical mechanics were evaluated using the velocity Verlet algorithm with a time step of 1.0 fs. The Nosé-Hoover thermostat for the NVT and NPT MD simulations uses a damping relaxation time of 0.1 ps and the dimensionless cell mass factor

of 1.0.

3.2 Construction and equilibration of the amorphous membrane

Using Cerius2's polymer builder and amorphous builder, a system containing 64 chains of Nafion each with an equivalent weight of 117. The simulation spaces are 3D periodic. Two systems are created, with approximately 10wt% and 20wt% water. The parameters of the the simulation cell are summarized in Table 1 and an illustration is provided in Figure 4. After the addition of the appropriate number of water molecules, atmospheric oxygen is added to the system. The oxygen molecules are added to regions of low density to allow for more rapid equilibration. The system is then equilibrated to simulate the movement and structure of the real-world material.

An annealing procedure is used to aid in overcoming local minima in the energy of the system. This *thermal-volume annealing* involves the use of 5 cycles of thermal annealing fluctuating between 300 and 600K then volume annealing the system between 0.5 and 1.1 times the experimental material density.

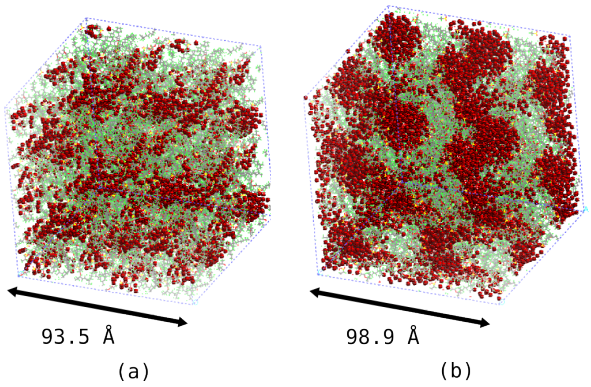

Figure 4: Structures of the as constructed (a) 10wt% and (b) 20wt% systems.

Table 1: Composition of hydrated Nafion membranes and simulation conditions

Equivalent weight	117	117
No. of chains	64	64
No. of O_2 molecules	8	8
Water content (wt %)	10	20
No. of water $(\lambda)^1$	4560(7)	9002(14)
Volume ($Å^3$)	8.18×10^5	9.67×10^5
Density (g/cm^3)	1.68	1.56

4 Results and Discussion

4.1 Distribution and solvation of oxygen

Upon completion of the simulation, the particles have reached a dynamic equilibrium for a given pressure and temperature. A useful way to analyze the position data is through the estimation of radial distribution functions. Radial distribution functions describe the density of particular objects as a function of the distance from another type of object. The RDF is usually designated $g(r)$ and probability density as $\rho(r)$. The expanded form of RDF is given in equation 1, where n_B is the number of particles of type B found in a shell shaped region of thickness δr and radius r concentric with particle A. N_B is the number of B particles in the system and V is the system volume.

$$g_{A-B}(r) = \frac{\rho(r)}{\rho_{global}} = \left(\frac{n_B}{4\pi r^2 \Delta r}\right) / \left(\frac{N_B}{V}\right) \tag{1}$$

Essentially, RDFs show the probability of finding one type of object at a particular distance from another type of object. An RDF for oxygen atoms to water atoms is shown in Figure 5.

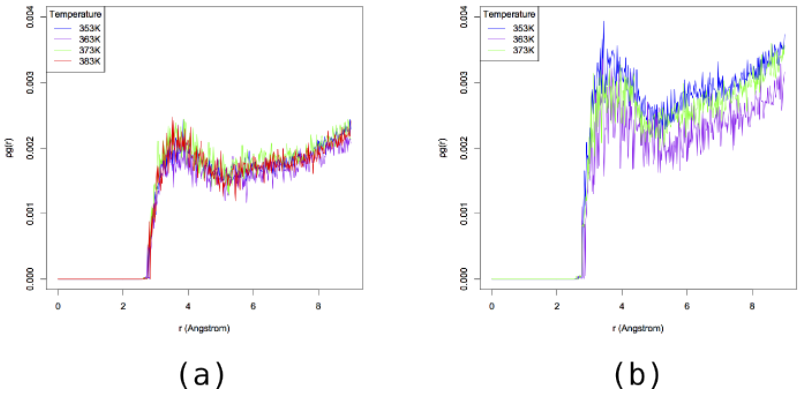

Figure 5: Pair correlation function of Water from Oxygen for (a) 10wt% and (b)20wt%.

The RDF model approximates the behavior of molecules within solvation shells found in a solution. A solvation shell is the volume containing the molecules acting as a solvent for a particular solute molecule. In the field of materials science these molecules are commonly referred to as the nearest neighbors of the solute molecule. Numerical integration of the radial distribution function yields the coordination numbers of molecules of interest. This is shown in equation (3) where N is the coordination number, R is the radius of the first solvation shell, and ρ is the global density of a particular particle.

$$N = 4\pi\rho \int_0^R g(r) r^2 \, dr \tag{2}$$

The results of this calculations for O2 - H2O are found in Figure 6 and Table 2. For all temperatures, the coordination in the 20wt% is higher than that of the 10wt%.

Table 2: Coordination number of oxygen with water in equilibrated system

		Temperature (K)			
		353	363	373	383
Weight %	10	0.783	0.727	0.819	0.794
	20	1.27	1.01	1.14	

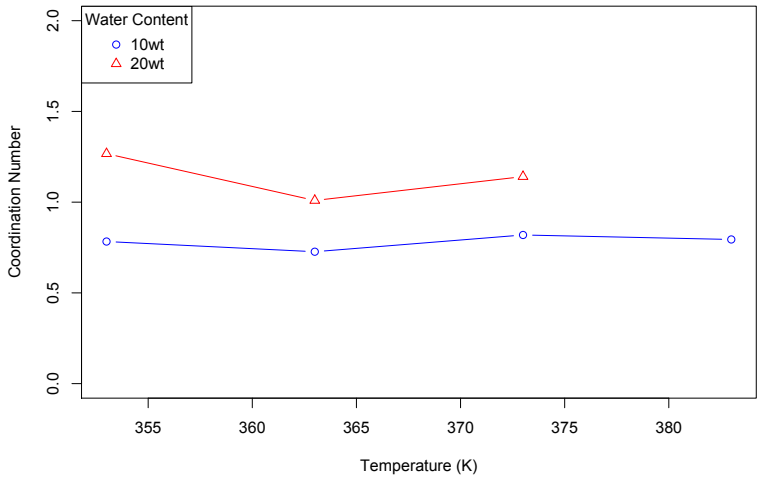

Figure 6: Coordination of oxygen with water with related to temperature and water content of the system.

4.2 Transport of oxygen

As the system equilibrates, the oxygen molecules will approach ideal diffusion conditions. The mean square displacement of the molecules is directly related to the diffusion coefficient of oxygen within the system at a particular temperature. Equation 3 describes this relationship.

$$D = \lim_{x \to \infty} \frac{1}{6t} \langle (r(t) - r(0))^2 \rangle \tag{3}$$

Notice that the 20wt% system has a lower coefficient of diffusion for all temperatures, shown in Figure 7, and a higher coordination with water, as shown in Figure 6.

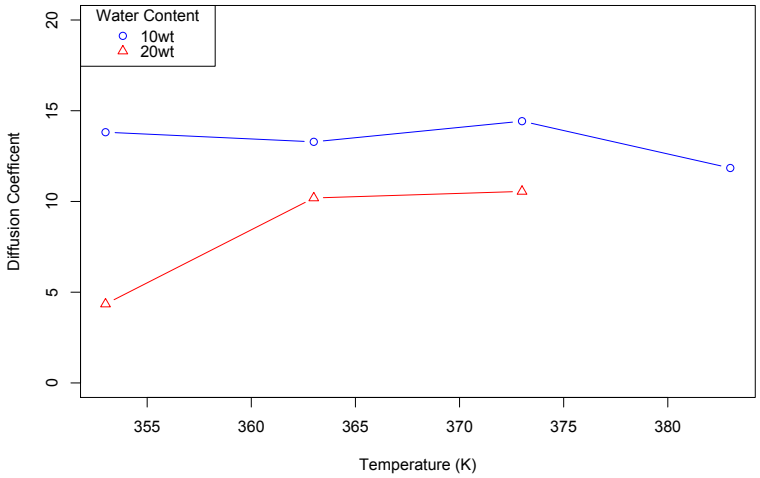

Figure 7: Diffusion coefficient of oxygen related to temperature and water content of the system.

Table 3: Diffusion coefficient of oxygen in equilibrated system

	Temperature (K)			
	353	363	373	383
Weight % 10	13.8	13.2	14.4	11.8
Weight % 20	4.35	10.2	10.6	

5 Conclusions

Through examination of oxygen in hydrated Nafion using fully atomistic molecular dynamics simulation several details become apparent. Oxygen appears to be hydrophobic in nature. As coordination of O2 with H2O increases the diffusion of oxygen decreases. The volume available for occupation by oxygen decreases as the water forms a continuous phase, as is the case in the 20wt% system. This correlation will be useful for determining the effect of oxygen transfer on fuel cell performance.

References

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